

The basics of quantum Monte Carlo

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Introduction

- Fundamental object in quantum mechanics:

$$\Psi(r_1, r_2, \dots, r_N)$$

- Want to find special wave functions such that

$$\hat{H}\Phi_n(r_1, r_2, \dots, r_N) = E\Phi_n(r_1, r_2, \dots, r_N)$$

where

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{iI} \frac{Z_I}{r_{iI}} + \sum_{i<j} \frac{1}{r_{ij}}$$

- This is a fundamentally many-body equation!
- We want to find an accurate method that will work in general to solve this

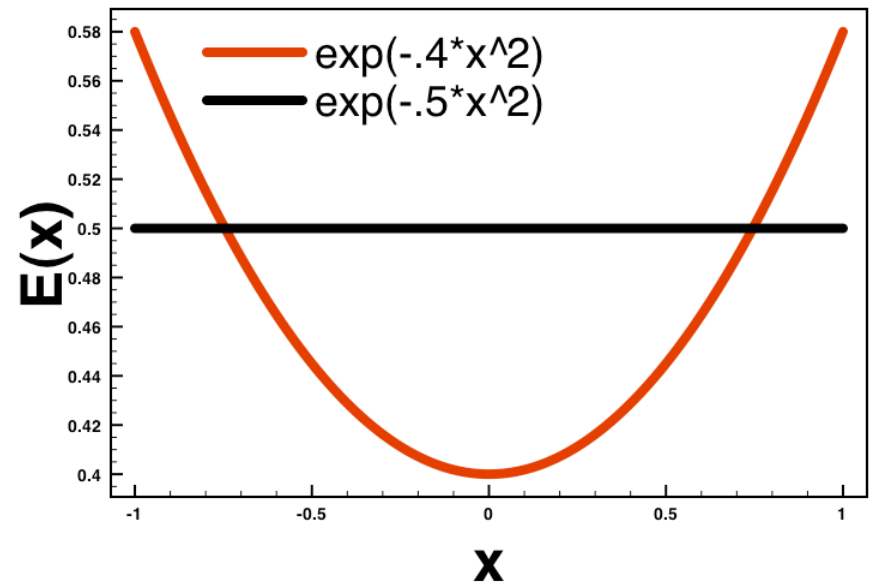
- Eigenvalue problem

$$\frac{\hat{H}\Phi_n(x)}{\Phi_n(x)} = E_n$$

- $E(x) = \frac{\hat{H}\Psi(x)}{\Psi(x)}$

- Non-eigenfunction and eigenfunction for simple harmonic osc.

- One way to approximate the eigenfunction: minimize deviation from a constant



- Solving a problem using random numbers!
- Evaluate integrals:
 - expectation value of a random variable is just the integral over its probability distribution
 - generate a bunch of random numbers and average to get the integral
- Simulate random processes--random walks sample configuration space
- Number of dimensions doesn't matter
- Statistical error!

- Comes in many flavors
- Deals with the many body wave function directly
work with $R=[r_1, r_2, \dots, r_n]$
- We'll cover two main flavors: variational Monte Carlo and diffusion Monte Carlo

- On 55 molecules, mean absolute deviation of atomization energy is 2.9 kcal/mol
- Successfully applied to organic molecules, transition metal oxides, solid state silicon, systems up to ~1000 electrons
- Can calculate accurate atomization energies, phase energy differences, excitation energies, one particle densities, correlation functions, etc..
- Scaling is from $O(1)$ to $O(N^3)$, depending on implementation and quantity.

Variational Monte Carlo

- Rewrite expectation value

$$E(P) = \int \frac{|\Psi(R,P)|^2}{\int |\Psi(R,P)|^2 dR} \frac{\hat{H}\Psi(R,P)}{\Psi(R,P)} dR$$

Probability distribution
function

- Idea: generate random walkers with probability equal to the above pdf and average (Metropolis method)
- Minimize the variance of the local energy with respect to the parameters

- General form of wave function

$$\Psi_T(R) = \text{Det}[\varphi_i(r_j)] \exp(U)$$

- Slater determinant (Hartree-Fock)

$$U = 0$$

- Two-body Jastrow

$$U = \sum_{il} \sum_k c_k^{ei} a_k(r_{il}) + \sum_{ij} \sum_k c_k^{ee} b_k(r_{ij})$$

- Three-body Jastrow

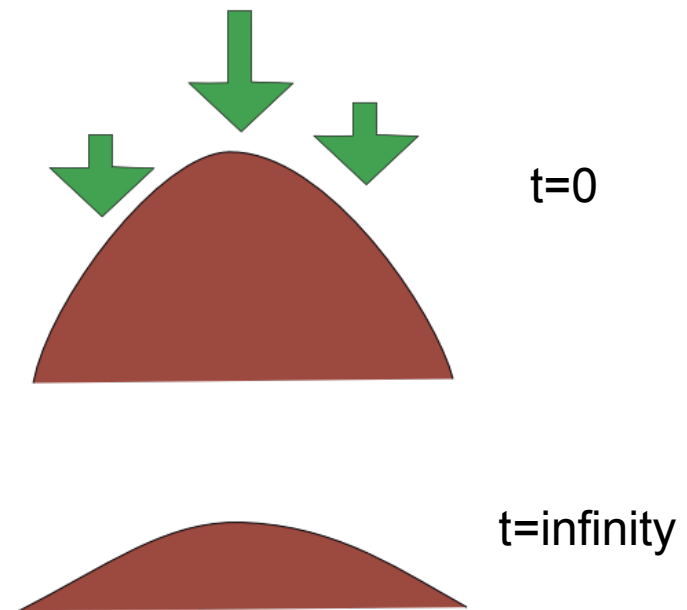
$$U = \text{two-body} + \sum_{ijl} \sum_{klm} c_{klm}^{eei} [a_k(r_{il})a_l(r_{jl}) + a_k(r_{jl})a_l(r_{il})] b_k(r_{ij})$$

- We optimize only the c coefficients

Diffusion Monte Carlo

- General strategy: stochastically simulate a differential equation that converges to the ground state
- Equation: $-\frac{d\Psi(R,t)}{dt} = (\hat{H} - E)\Psi(R,t)$
- Must propagate an entire function forward in time
<=> distribution of walkers

- We want to find a wave function so $\hat{H}\Psi = E\Psi$
- Our differential equation $-\frac{d\Psi(R,t)}{dt} = (\hat{H} - E)\Psi(R,t)$
- Suppose that $\left(-\frac{1}{2}\nabla^2 + V(R)\right)\Psi > E\Psi$
- $|\Psi|$ decreases
- Kinetic energy (curvature) decreases, potential energy stays the same
- Time derivative is zero when $\hat{H}\Psi = E\Psi$



$$-\frac{d\Psi(R,t)}{dt} = -\frac{1}{2}\nabla^2\Psi(R,t) + (V(R) - E)\Psi(R,t)$$

Diffusion
Birth/death

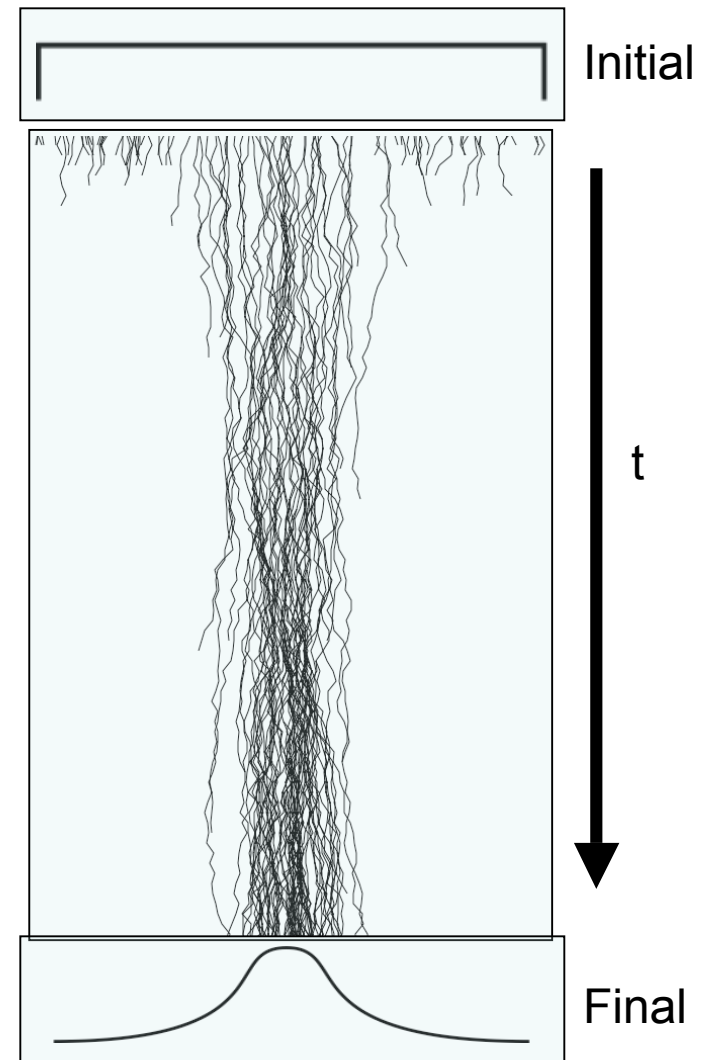
- Generate walkers with a guess distribution

- Each time step:

- Take a random step (diffuse)
- A walker can either die, give birth, or just keep going

- Keep following rules, and we find the ground state!

- Works in an arbitrary number of dimensions



- Importance sampling: multiply the differential equation by a trial wave function
 - Converges to $\Psi_T \Phi_0$ instead of Φ_0
 - The better the trial function, the faster DMC is-- feed it a wave function from VMC
- Fixed node approximation: for fermions, ground state has negative and positive parts
 - Not a pdf--can't sample it
 - Approximation: $\Psi_T \Phi_0 > 0$

- Choose system and get one-particle orbitals (we've already prepared the orbitals for you)
- Optimize wave function using VMC, evaluate energy and properties of wave function
- Use optimized wave function in DMC for most accurate, lowest energy calculations
- Check the tooltips for explanations of the few settings

- The pair correlation function for the Slater determinant and optimized two-body wave functions, also compare with DMC
- The relative energies of Slater determinant/two-body wave function/DMC.
- The fluctuations in the trace of the Slater determinant versus two-body wave function.

- Hammond, Lester, and Reynolds. Monte Carlo Methods in Quantum Chemistry (book)
- Wikipedia, www.qwalk.org, www.qmcwiki.org
- Foulkes, Mitas, Needs, and Rajagopal. Rev. Mod. Phys. **73**, 33 (2001)
- Umrigar, Nightingale, and Runge. J. Chem. Phys. **99**, 2865 (1993)